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# Charge Exchange Cross Sections for Argon Ions in $H_2$ and $D_2$ below 1 KeV*

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## ABSTRACT

Charge exchange cross sections for $Ar^+$ ions incident on hydrogen and deuterium have been measured over the energy range of 30 to over 1000 eV. The argon ion beam was formed by electron bombardment and electrostatic acceleration. Ionizing electron energy was nominally 18 eV, although the results appeared to be insensitive to this parameter. The measured cross sections for $Ar^+ + H_2 \longrightarrow Ar + H_2^+$ as a function of ion energy are compared with the results of other investigators, which are in rather

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poor agreement. The measurements confirm that the cross section exhibits a maximum at approximately 180 eV incident ion energy. Theoretical calculations by Gurnee and Magee and by Karmohapatro are discussed for this reaction. The cross section for $Ar^+ + D_2 \longrightarrow Ar + D_2^+$ was also found to exhibit a maximum, but at approximately 85 eV, which is nearly the same center-of-mass energy as for the $H_2$ target. The possible influence of ion-molecule reactions on the charge transfer cross sections is discussed.

## INTRODUCTION

Charge exchange cross sections for low energy argon ions in molecular hydrogen are of interest for several reasons. The study we report here of this cross section arose because of the interest in obtaining a neutral argon beam for ionization studies at low energies.[1] By obtaining a neutral beam in this manner, one can be assured that no metastable argon atoms will arise below 240 eV beam energy, since the center-of-mass energy for the $Ar^+ + H_2$ charge-exchanging collisions is only 1/21 of the incident ion energy. In addition, this cross section is of considerable theoretical interest. Both the measurements performed by Wolf[2] and by Gilbody and Hasted,[3] while differing considerably in

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[1] R. C. Amme and H. C. Hayden, J. Chem. Phys. 44(1966) (to be published).

[2] F. Wolf, Ann. der Phys. 27, 543(1936).

[3] H. B. Gilbody and J. B. Hasted, Proc. Roy. Soc. A238, 334(1957).

magnitude, show a maximum in the cross section in the neighborhood of 200 eV. Since the cross section is non-resonant, one may expect on the basis of the adiabatic criterion that a maximum may appear at high energy if the $H_2^+$ ion is formed in the ground vibrational state, but at much lower energy if it is formed in the v=1 state. A theoretical treatment, while complicated for the scattered wave method, is possible with the semi-classical impact parameter method. Hence, this cross section also has been studied theoretically: by Gurnee and Magee,[4] and by Karmohapatro and Das.[5,6] Gurnee and Magee considered the reaction in which the hydrogen molecular ion is left vibrationally excited, and found a theoretically large cross section with a predicted maximum at about 20 eV. Karmohapatro, using an improved wave function, attempted to obtain closer agreement with experiment. We shall return to this work later (see Discussion).

The $Ar^+ + D_2$ charge exchange process is also of interest, because there are distinct differences from, and similarities to, the case of hydrogen. The c.m. energies differ for the two cases by a factor of 1.9 at a given beam energy. The ionization potential differs slightly[7]

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[4] E. F. Gurnee and J. L. Magee, J. Chem. Phys. 26, 1237(1957).

[5] S. B. Karmohapatro and T. P. Das, J. Chem. Phys. 29, 240(1958).

[6] S. B. Karmohapatro, J. Chem. Phys. 30, 538(1959).

[7] V. H. Dibeler, R. M. Reese, and M. Krauss, J. Chem. Phys. 42, 2045(1965).

from that for $H_2$, and the vibrational (and rotational) levels of the $D_2^+$ ion are more closely spaced. The energy defects for the two charge transfer reactions will differ only slightly for the v=o cases but considerably more, relatively, for excited vibrational states.

## APPARATUS

The argon ion beam was formed by electron impact and electrostatic acceleration. The ion source design is that described by Utterback and Miller.[8] A tungsten wire filament is used with a heating voltage of 3.6v. The argon utilized was of high purity, and the resultant ion beam was better than 99% pure as determined by a quadrupole spectrometer. Contaminants were a few tenths percent water vapor and $N_2^+$. Operating pressure was typically 20 mtorr. In Fig. 1, a plot is shown of the extracted ion current, normalized to total ionizing electron current, as a function of the ion-source voltage read from an accurate voltmeter. The break-point is found to be at 17.8 volts. The offset of the electron energy of approximately 2 volts from the 15.755 eV appearance potential for $Ar^+(^2P_{3/2})$ ground state ions is reasonable, considering the 1.8 V elevation of the center of the filament above the ion source case and the thermal electron energy. The presence of some $Ar^+(^2P_{\frac{1}{2}})$ is also expected, since this state lies at 15.932 eV (spectroscopic value). An electron energy of about 18 eV was used for most of the measurements in order to obtain adequate ion current. Ion energy spread with this type source is small.[8]

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[8] N. G. Utterback and G. H. Miller, Rev. Sci. Instr. 32, 1101(1961).

The charge transfer cell is shown in Fig. 2. Its operation has been described in other papers,[8,9] and will be discussed only briefly here. The entire system was evacuated by liquid-nitrogen trapped mercury diffusion pumps to a pressure of a few times $10^{-7}$ torr. All electrodes are gold plated. The small filament at the top of the assembly is used to reduce the accumulation of charge on the entrance aperture and to improve beam focus and stability. The final exit aperture is fitted with a tube which leads to a dry-ice trapped McLeod gauge and also to an MKS Baratron capacitance manometer.[10] The two types of pressure measurement were in good agreement, as to be expected with hydrogen. Typical neutralizing pressure was about 0.1 mtorr.

The transfer cell consists of a cylindrical grid of 0.0007 in. gold-covered wire maintained at ground potential. The grid is surrounded by a concentric cup whose potential may be held positive with respect to the grid to repel the slow ions arising from charge transfer. The slow ions are then collected on the grid as $i_3$, while scattered ions with sufficient energy are collected on the cup as $i_2$. The fast ions which do not become scattered or undergo charge exchange are measured on the

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[9] R. C. Amme and H. C. Hayden, J. Chem. Phys. 42, 2011(1965).

[10] A comprehensive study of the accuracy of this type instrument has been described by N. G. Utterback (submitted to Rev. Sci. Instr.) and also by P. Rony, Lawrence Radiation Laboratory Report UCRL-11218, Pt.II, Berkeley, California(1965).

ion collector as the current $i_1$. The fraction $i_2/i_3$ indicates the ratio of the scattering probability to the charge-transfer probability. The sum $i_2 + i_3$ is typically 15% of the total incident beam current $i_1 + i_2 + i_3$. The ratio of the grid current, $i_3$, to the total incident current is called $\beta$. The measurement of $\beta$ as a function of the cup potential constitutes an approximate energy analysis of the slow and scattered ions. Figure 3 presents typical analyses for the two cases. The sudden rise of current with increasing cup potential corresponds to those $H_2^+$ and $D_2^+$ ions which have been formed with little momentum transfer. The nearly constant slope at higher cup potentials corresponds to scattered ions. The slope is, for these target gases, very gentle and the breakover is quite distinct, so that extrapolation of the linear portion of the curves back to zero cup potential can be performed without ambiguity. The charge transfer cross sections are obtained from this extrapolated value. The quantity $\beta/P$, where P is the neutralizing gas pressure, is proportional to the charge exchange cross section, $\sigma_q$. If P is in units of mtorr the conversion factor to square angstroms is 76.3.

## RESULTS

In Fig. 4 we have plotted the charge exchange cross section $\sigma_q$ for the process $Ar^+ + H_2 \longrightarrow Ar + H_2^+$. Each point is a result of an energy analysis of the type seen in Fig. 3. Shown for comparison are the measurements by Gilbody and Hasted,[3] Wolf,[2] and by Ghosh and Sheridan.[11]

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[11] S. N. Ghosh and W. F. Sheridan, J. Chem. Phys. 26, 480(1957). Not shown are some measurements by Gustafsson and Lindholm (Ark. Fys. 18, 219(1961)) who obtained cross sections less than $10 Å^2$.

There is good agreement between our own data and those of the latter authors. Both results show that the cross section is fairly insensitive to energy above 300 eV. In particular, we observe a cross section which is nearly constant from 250 to 1100 eV and about 17% greater than that of Ghosh and Sheridan. A gentle maximum is observed at about 175 eV. A maximum in this region is in reasonable agreement with all other data. A pronounced decrease is observed below 100 eV.

Results of the measurements for the process:

$$Ar^+ + D_2 \longrightarrow Ar + D_2^+$$

are shown in Fig. 5, along with the $H_2$ process from Fig. 4 for comparison. The cross section involving deuterium is found to be more dependent upon ion energy and crosses through that for $H_2$. The maximum, which occurs at about 85 eV, is considerably more pronounced.

A measurement at 2400 eV (not shown) gave a cross section of $9.3\text{Å}^{o2}$, indicating further decrease in $\sigma_q$ with increasing energy.

## DISCUSSION

Because of the low ionizing electron energy used in this work, the ion beam consists only of $^2P_{1/2}$ and $^2P_{3/2}$ ions, perhaps in the ratio of 2J+1 (1:2) or higher. To determine whether the ionizing electron energy was an important factor, we varied this parameter over a wide range from just above threshold, namely 16 eV, to over 40 eV. This was done at both high and low beam energies, and for $D_2$ and $H_2$ targets. No very significant effects were observed. In Fig. 6 we have plotted the ratio $\beta/P$,

obtained with the cup at 10 v, as a function of ionizing electron energy, and using a 50 eV ion beam with $H_2$ target gas. Variations were typically on the order of 5%. At low electron energies ($\lesssim$17 eV) the beam intensity is also low, and the values of $\beta$ less precise.

With the presence of both J = 3/2, 1/2 argon ions, we have several near-resonant processes possible for $H_2^+(v=0, 1, 2)$:

(1) $Ar^+(J=3/2) + H_2 \longrightarrow Ar + H_2^+(v=0) + 0.328$ eV;

(2) $\longrightarrow Ar + H_2^+(v=1) + 0.059$ eV;

(3) $\longrightarrow Ar + H_2^+(v=2) - 0.195$ eV;

(4) $Ar^+(J=\frac{1}{2}) + H_2 \longrightarrow Ar + H_2^+(v=0) + 0.505$ eV;

(5) $\longrightarrow Ar + H_2^+(v=1) + 0.236$ eV;

(6) $\longrightarrow Ar + H_2^+(v=2) - 0.018$ eV.

For the deuterium target (v=0,1,2):

(7) $Ar^+(J=3/2)+D_2 \longrightarrow Ar + D_2^+(v=0) + 0.291$ eV;

(8) $\longrightarrow Ar + D_2^+(v=1) + 0.096$ eV;

(9) $\longrightarrow Ar + D_2^+(v=2) - 0.091$ eV;

(10) $Ar^+(J=\frac{1}{2}) + D_2 \longrightarrow Ar + D_2^+(v=0) + 0.468$ eV;

(11) $\longrightarrow Ar + D_2^+(v=1) + 0.273$ eV;

(12) $\longrightarrow Ar + D_2^+(v=2) + 0.086$ eV.

In the latter case, considering also v=3, we have

(13) $Ar^+(J=\frac{1}{2}) + D_2 \longrightarrow Ar + D_2^+(v=3) - 0.094$ eV.

In calculating the above energy defects for infinite separation we have used the spectroscopic values for ionization potentials:[12] $Ar^+(^2P_{3/2})$, 15.755 eV; $Ar^+(^2P_{\frac{1}{2}})$, 15.932 eV; $H_2^+(v=0)$, 15.427 eV; $D_2^+(v=0)$, 15.464 eV. The latter value is that reported by Dibeler, Reese and Krauss.[7] To obtain the vibrational levels for $H_2^+$ we have included the anharmonicity factor,[13] $\omega_e x_e$, which contributes 0.015 eV in Reaction (2). With these more precise values we find for this reaction an energy defect of 0.059 eV, in contrast to the 0.04 eV used by Gurnee and Magee.[4] This difference of nearly 50% would move the position of their calculated maximum to higher energy and reduce the overall cross section to give better agreement with experiment. Karmohapatro[6] also used an energy defect of +0.04 eV in his calculations, and obtained a maximum in the cross section at about 40 eV for Reaction (2). The cross sections that he obtained for Reactions (4) and (5) appear to agree well with experiment. However, the energy defects employed were in serious error. Higher vibrational states were not considered. The Franck-Condon factors for $H_2^+$ observed by photoabsorption[14] indicate the importance of Reaction (6) as well: the higher cross sections obtained by Gilbody and Hasted, together with their results for $Ar^+$ in Ar, which also exhibited a maximum near 150 eV, suggest a higher concentration of the $^2P_{\frac{1}{2}}$ state for their beam. By contrast, the cross section for this symmetric reaction as measured with our beam shows a resonant behavior.[9]

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[12] R. W. Kiser, Tables of Ionization Potentials USAEC Report TID-6142, Office Of Tech. Serv., Dept. of Commerce, Wash., D.C.(1960).

[13] G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc., Princeton, N.J., 1950) P.92.

For the case of $D_2^+$, we have used the vibrational energies calculated by Dunn.[14] In all these arguments, rotational transitions have been neglected.

We note also that the adiabatic criterion: $a|\Delta E| \simeq h\nu_{max}$, which provides an estimate of the relative velocity at the maximum $Q_q$ in terms of the interaction distance $\underline{a}$, may be written: $E_{max} \simeq 3a^2M(\Delta E)^2$, with the energies E and $\Delta E$ in eV, $\underline{a}$ in angstrom units and M as the atomic weight of the incident ion. For Reaction (1), the observed maximum at 180 eV would yield the value: $a \simeq 4$ Å. However, if this value were valid for both $H_2$ and $D_2$ targets, the corresponding maximum for $D_2$, Reaction (7), would be found at about 140 eV.

The relative populations of $D_2^+$ vibrational states for direct ionization[14] are large for the v=2,3,4 states, suggesting the importance of Reaction (9) and possibly (12), (13). However, none of these has an energy defect as small as Reactions (2) and (6) involving $H_2^+$ (v=1,2), for which the Franck-Condon factors are also large.

In terms of the center-of-mass energy, the maxima for the two processes in Fig. 5 occur at nearly the same place, namely 8 eV. Geise and Maier[15] have studied the ion-molecule reaction:

$$Ar^+ + D_2 \longrightarrow ArD^+ + D.$$

At a c.m. energy of 8 eV, the cross section for this reaction may be as high as a few square angstroms, and at 35 eV lab (3.2 eV c.m.), on the

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[14] G. H. Dunn, J. Chem. Phys. 44, (1966) (April issue).

[15] C. F. Giese and W. B. Maier II, J. Chem. Phys. 39, 739(1963).

order of 10 $\mathring{A}^2$. Thus, the rise in the charge exchange cross section appears to precede the ion-molecule reaction, and at low c.m. energies, $\sigma_q$ gives way to this competing process.

The presence of the ion-molecule reaction should not affect our measurements adversely. The $ArH^+$ and $ArD^+$ ions which may be formed will carry considerable kinetic energy, and if they are not scattered into the cup, they will be collected as $i_1$ and cannot contribute significantly to the slow ion current. As a check on the validity of this remark, we have used the neutral beam formed in the charge transfer to re-examine the ionization cross section for argon atoms on argon atoms.[16] Preliminary results indicate very good agreement with the cross sections obtained by neutralizing the beams in argon. This work will be described in a later paper.

## ACKNOWLEDGMENTS

The authors are indebted to Messrs. H. C. Hayden and P. O. Haugsjaa for laboratory assistance.

[16] H. C. Hayden and R. C. Amme, Phys. Rev. 141, 30(1966).

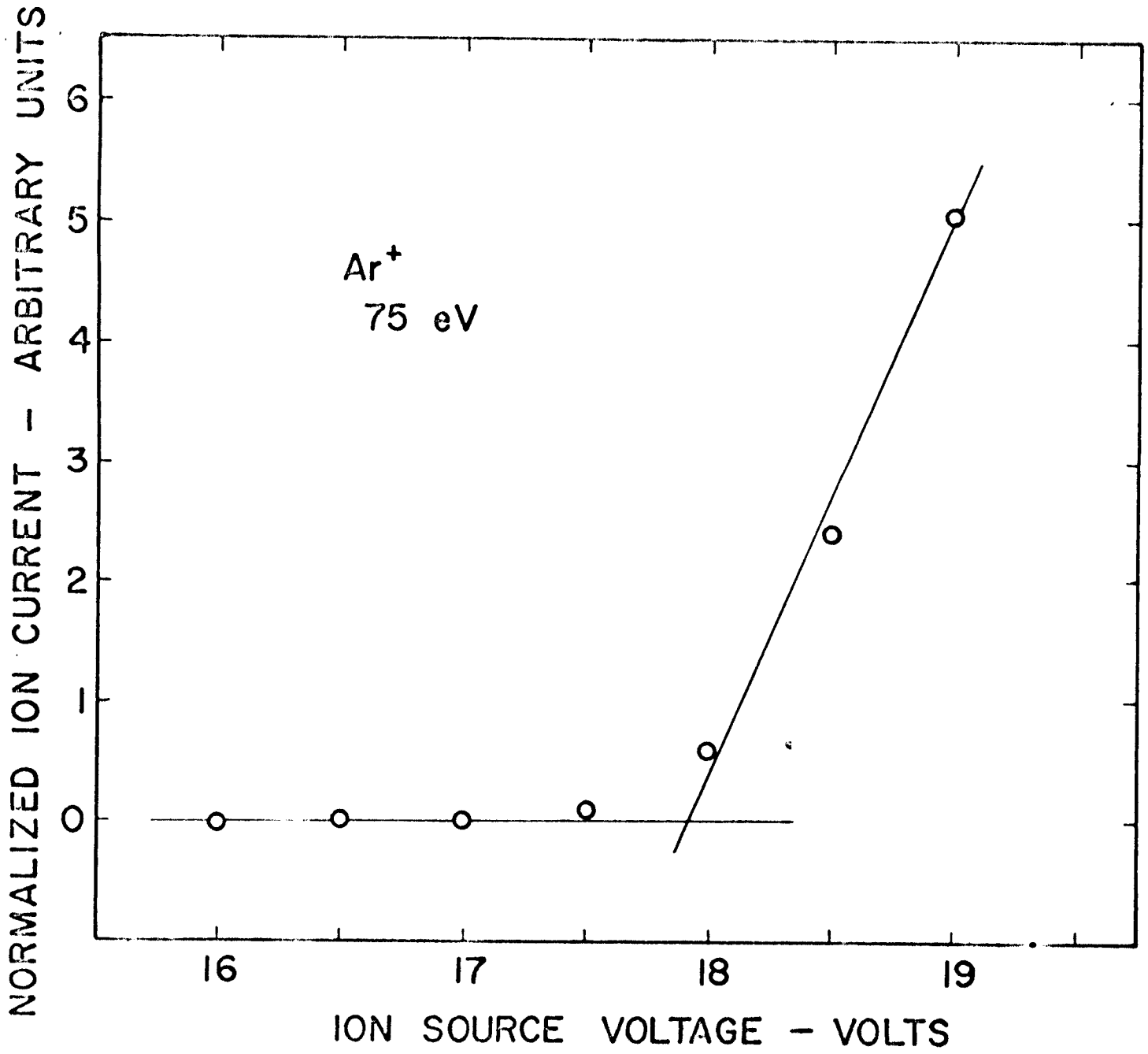


Fig. 1. Ion Source Calibration with Argon

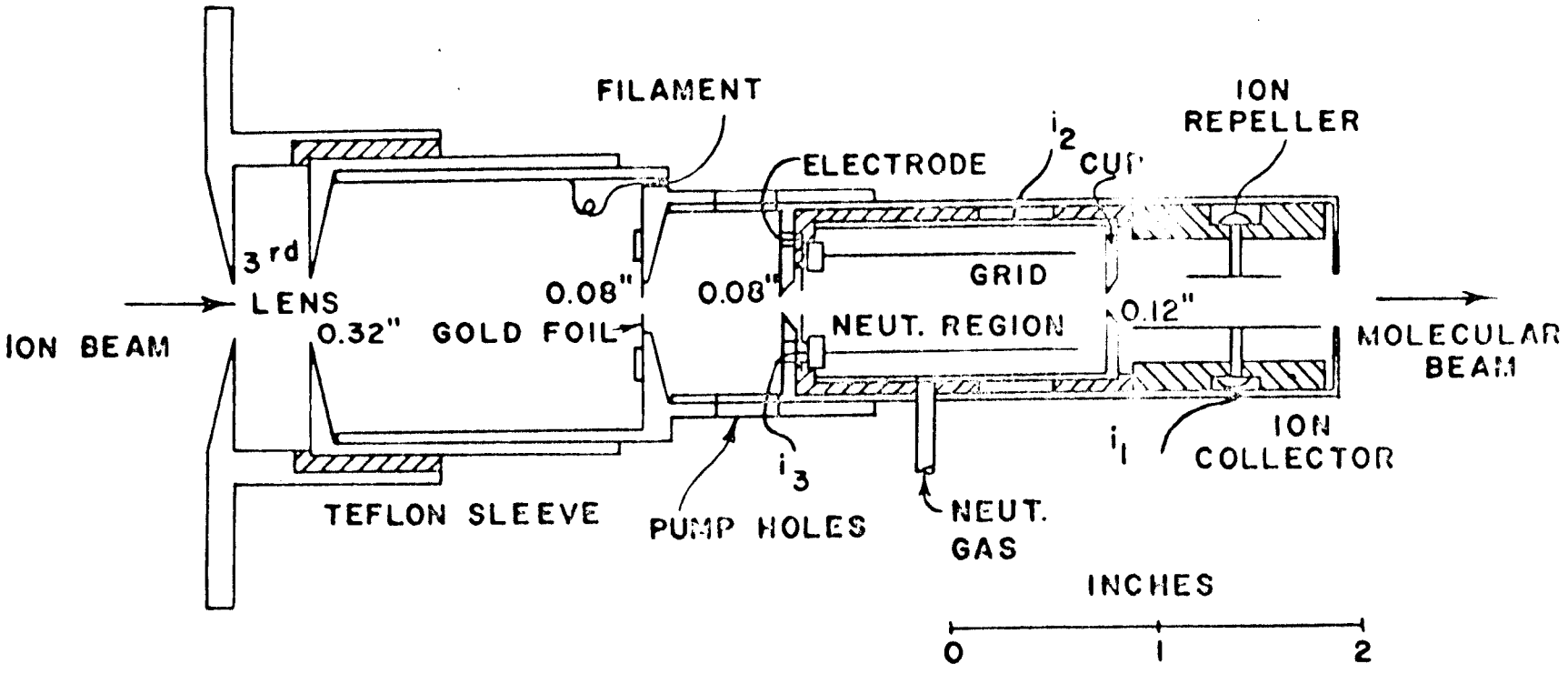


Fig. 2. Charge Transfer Cell.

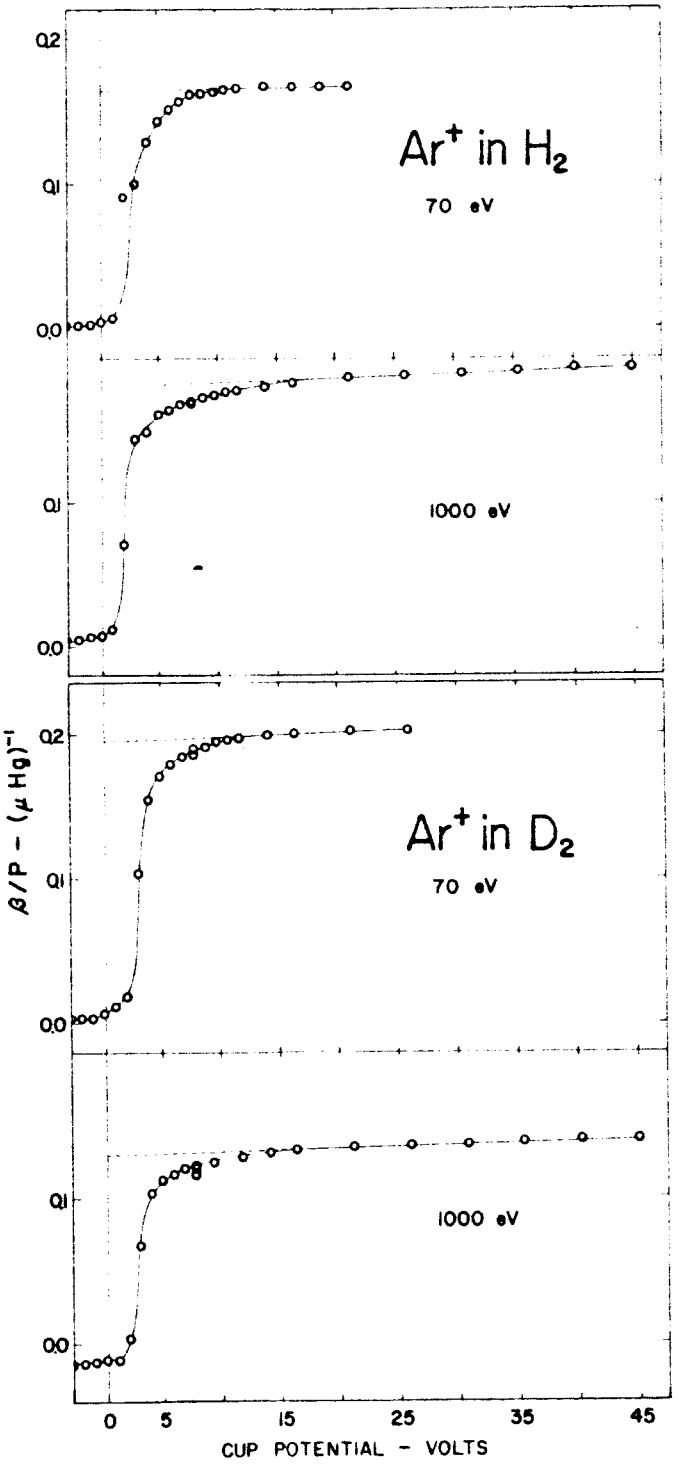


Fig. 3. Ratio β/P vs cup potential. Top pair is for $H_2$ target; bottom pair for $D_2$ target.

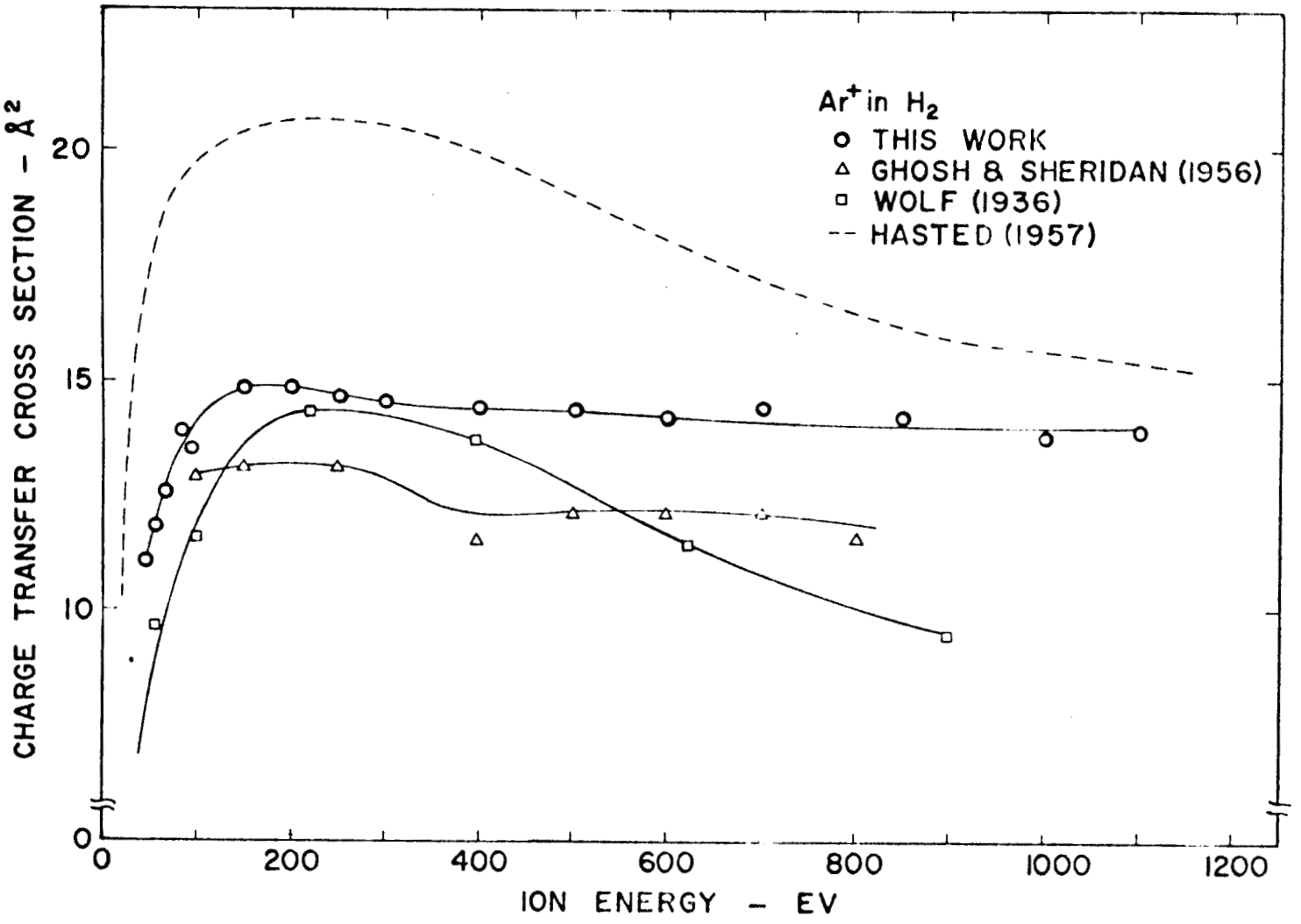


Fig. 4. $Ar^+ + H_2$ Charge-Transfer Cross Section as a function of ion energy compared with measurements of other investigators.

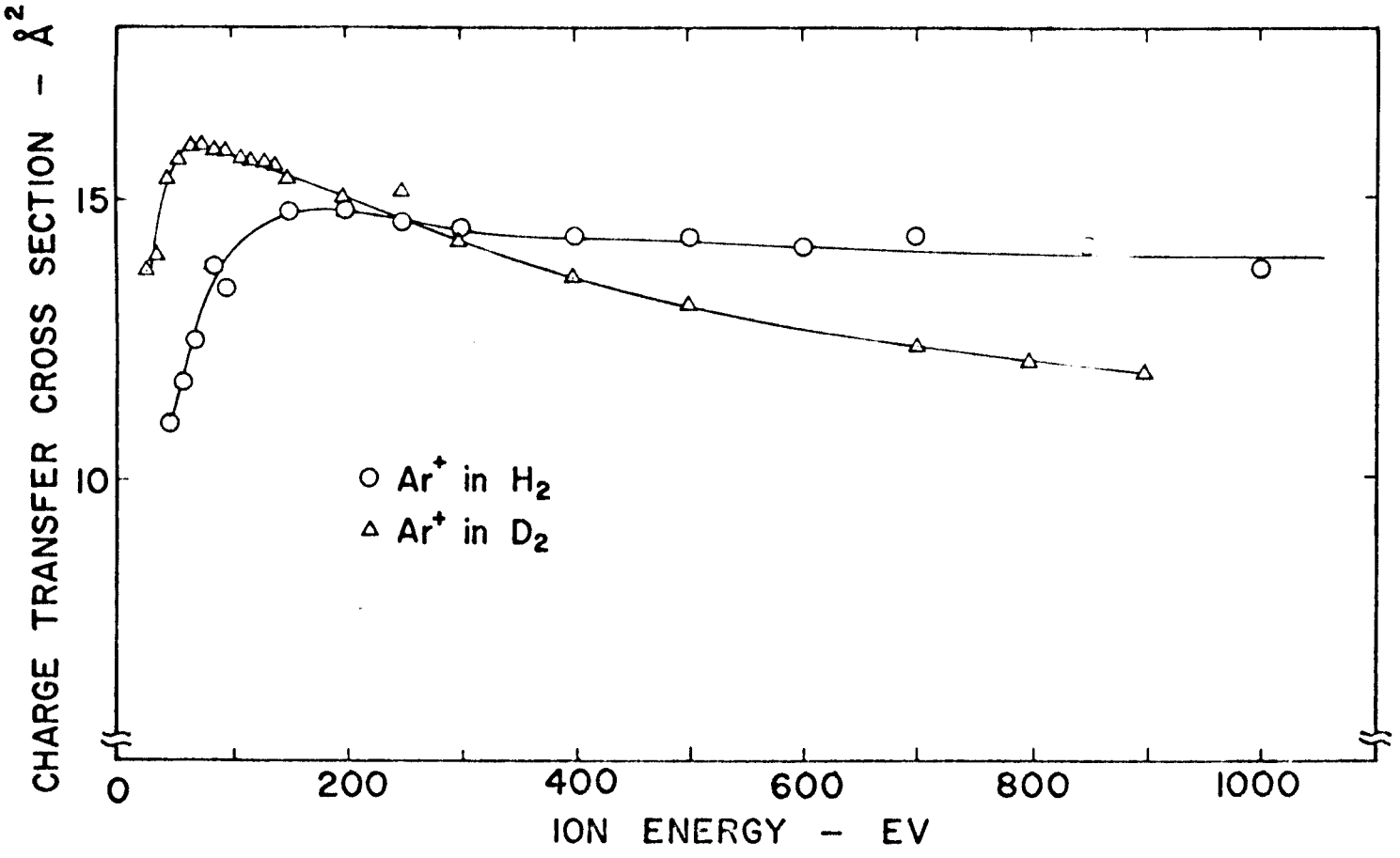


Fig. 5. Comparison of Charge-Transfer Cross Sections for $Ar^+$ ions in $H_2$ and in $D_2$ as a function of ion energy.

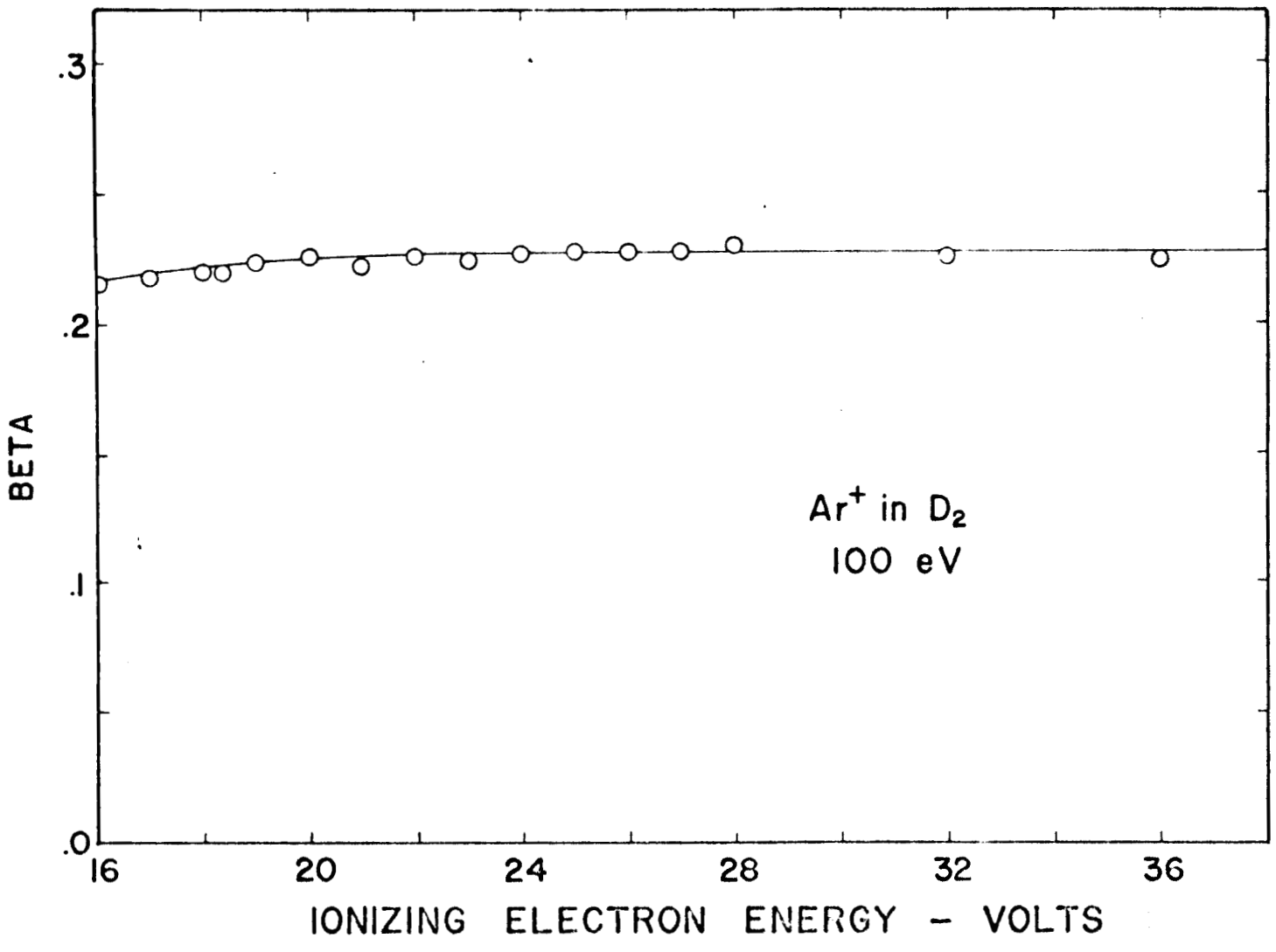


Fig. 6. Effect of Varying Ionizing Electron Energy on the Charge-Exchange Cross Section for $Ar^+ + D_2$.